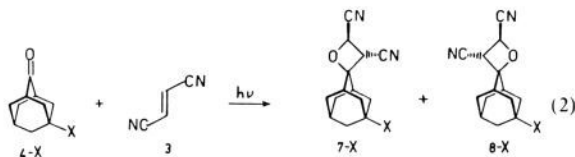


Figure 1. ORTEP structure of 7-X.

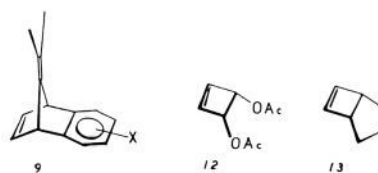
Irradiation at 313 nm of a solution of 1 g of **3** and 0.5 g of **4-X** in 50 mL of spectrograde acetonitrile for 48 h leads<sup>13</sup> to the formation of *trans*- and *cis*-oxetanes and to the *cis*-*trans* isomerization of **3**. At low conversions only *trans*-oxetanes were formed (eq 2). After workup the solution gave residues that could be



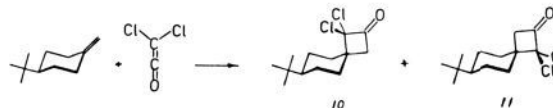
separated by column chromatography to give **7-X** and **8-X** ( $\geq 80\%$  chemical yield by means of either VPC or NMR integration). In all instances examined ( $X = F, Cl, Br, OH$ ), the major isomer ( $\sim 60:40$ ) was **7-X** (see Table I).

The structural assignments were determined by means of <sup>13</sup>C NMR; the chemical shifts of both isomers could be calculated on the basis of those of 7-H and those of adamantane itself in the manner described above. The question of *cis*- or *trans*-nitrile group configuration was determined from the magnitudes of the coupling constants for the oxetane ring protons: they fall within the range 5.5–5.8 Hz, consistent with *trans* configurations.<sup>14</sup> Finally, the configuration of **7-F** was established independently by means of an X-ray diffraction study (see Figure 1).<sup>15</sup>

In the Diels–Alder reaction, the diene functions as the donor; in the photocycloadditions, the carbonyl  $\pi^*$  state is the nucleophile. Although the mechanisms of the two cycloadditions are different, one being a concerted thermal process and the other involving an exciplex, we believe that bond formation in both cases is assisted by  $\sigma$  delocalization of the electron richer bonds anti to the 5-substituent into the incipient  $\sigma^*$  orbital and that these reactions constitute further evidence for the generality of the rule stated above. We note that several other cycloadditions already in the literature exhibit stereoselectivities explicable on the same basis: these include the Diels–Alder reactions of **9**,<sup>16</sup> the contra-steric



axial [2 + 2] cycloaddition of dichloroketene to methylene-cyclohexane to give **10** and **11** in 4:1 ratio,<sup>17,18</sup> and the contrasting stereochemistry of [1,3]-dipolar cycloaddition of diazomethane to **12** (100% *syn*) and **13** (100% *anti*).<sup>19</sup> The explanations offered or discussed were in all instances different from our own.



While we do not wish to assert the hyperconjugation has no rivals as the basis of these effects, it is noteworthy that the rule serves as a simple heuristic device that correctly anticipates the stereochemistry in both thermal and photochemical reactions: bond formation occurs at the face anti to the most electron rich  $\sigma$  bond. This rule can be readily employed to make predictions for the whole, rich variety of pericyclic reactions, and we shall report our results of studies aimed at determining their stereoselectivities in due time.

**Acknowledgment.** This work was supported at Columbia by the NSF and the AFOSR and at Stony Brook by the NSF and the Petroleum Research Fund; we thank the donors of this fund.

**Supplementary Material Available:** Tables of <sup>13</sup>C and <sup>1</sup>H NMR data of all compounds mentioned in this paper and X-ray data for compound **7-X** (21 pages). Ordering information is given on any current masthead page.

(16) (a) Okada, K.; Mukai, T. *J. Am. Chem. Soc.* **1978**, *100*, 6509. (b) Paquette, L. A.; Hertel, L. W.; Gleiter, R.; Bohm, M. *J. Am. Chem. Soc.* **1978**, *100*, 6510.

(17) Dunkelblum, E. *Tetrahedron* **1978**, *32*, 975.  
(18) Picard, P.; Moulines, J.; Lecoustre, M. *Bull. Chem. Soc. Fr.* **1984**, II-65.  
(19) Burdisso, M.; Gandolfi, R.; Lucchi, M.; Rastelli, A. *J. Org. Chem.* **1988**, *53*, 2125.

## Specific Deuterium Isotope Effects on the Rates of Electron Transfer within Geminate Radical-Ion Pairs

Ian R. Gould\* and Samir Farid\*

Eastman Kodak Company, Corporate  
Research Laboratories, 1999 Lake Avenue  
Rochester, New York 14650-2109

Received July 28, 1988

Recent theories of electron-transfer reactions treat the rear-ranged high-frequency ( $h\nu > kT$ ) internal vibrational modes quantum mechanically, whereas the low-frequency solvent modes are treated classically.<sup>1</sup> The role of quantum effects in the internal reorganization can, in principle, be investigated by the study of isotope effects. The Franck–Condon factors for electron transfer depend upon vibrational overlap and are proportional to the frequencies of the vibrational modes involved in the transition. Thus, isotopic substitution, which modifies these frequencies, should affect the reaction rate. Several examples of isotope effects

(12) (a) Schuster, G. B.; Turro, N. J.; Steinmetzer, H.-C.; Schaap, A. P.; Faler, G.; Adam, W.; Liu, J. C. *J. Am. Chem. Soc.* **1975**, *97*, 7110. (b) Dalton, J. C.; Wriede, P. A.; Turro, N. J. *J. Am. Chem. Soc.* **1970**, *92*, 1318.  
(13) Kahn, S. D.; Hehre, W. J. *J. Am. Chem. Soc.* **1987**, *109*, 663.  
(14) (a) Turro, N. J.; Wriede, P. A. *J. Org. Chem.* **1969**, *34*, 3562. (b) Bartrop, J. A.; Carless, H. A. *J. Am. Chem. Soc.* **1972**, *94*, 1951.  
(15) All compounds mentioned in this paper have been completely characterized (see Supplementary Material).

(1) (a) Hopfield, J. J. *Proc. Natl. Acad. Sci. U.S.A.* **1974**, *71*, 3640. (b) Van Duyne, R. P.; Fischer, S. F. *Chem. Phys.* **1974**, *5*, 183. (c) Ulstrup, J.; Jortner, J. *J. Chem. Phys.* **1975**, *63*, 4358. (d) Siders, P.; Marcus, R. A. *J. Am. Chem. Soc.* **1981**, *103*, 741, 748. (e) Brunschweig, B. S.; Logan, J.; Newton, M. D.; Sutin, N. *J. Am. Chem. Soc.* **1980**, *102*, 5798.

**Table I.** Rate Constants for Return Electron Transfer from Cyanoanthracene Radical Anions to Deuteriated and Nondeuteriated Methyl-Substituted Benzene Radical Cations in Acetonitrile at 25 °C

radical cation	radical anion <sup>a</sup>	$-\Delta G_{\text{et}}^b$	$k_d (\times 10^{-9} \text{ s}^{-1})$	$k_h (\times 10^{-9} \text{ s}^{-1})$	$k_h/k_d$	$(k_h/k_d)_{\text{perMe}}^c$
toluene	TCA	<i>d</i>	1.88	1.50	1.253	1.253
1,2,3,5-tetramethyl benzene	DCA	2.77	0.80	1.32	1.659	1.135
durene	DCA	2.72	0.98	1.59	1.627	1.129
<i>m</i> -xylene	TCA	2.58	2.97	3.66	1.237	1.112
<i>o</i> -xylene	TCA	2.57	2.96	3.63	1.227	1.108
mesitylene	TCA	2.55	3.77	4.93	1.312	1.095
hexamethylbenzene	DCA	2.53	3.12	5.60	1.796	1.103
<i>p</i> -xylene	TCA	2.50	4.60	6.00	1.299	1.140
1,2,3,5-tetramethylbenzene	TCA	2.27	9.75	11.69	1.20	1.047
durene	TCA	2.22	10.18	12.33	1.21	1.049
hexamethylbenzene	TCA	2.03	14.42	15.89	1.10	1.017

<sup>a</sup>DCA = 9,10-dicyanoanthracene, TCA = 2,6,9,10-tetracyanoanthracene. <sup>b</sup>Calculated from  $E_{\text{red}}(\text{A}) - E_{\text{ox}}(\text{D})$  in which A = cyanoanthracene and D = methyl-substituted benzenes (ref 8). <sup>c</sup>Calculated according to eq 2. <sup>d</sup>The electrochemical oxidation of toluene is not reversible (ref 10), and so the value of  $\Delta G_{\text{et}}$  for this reaction cannot be accurately obtained.

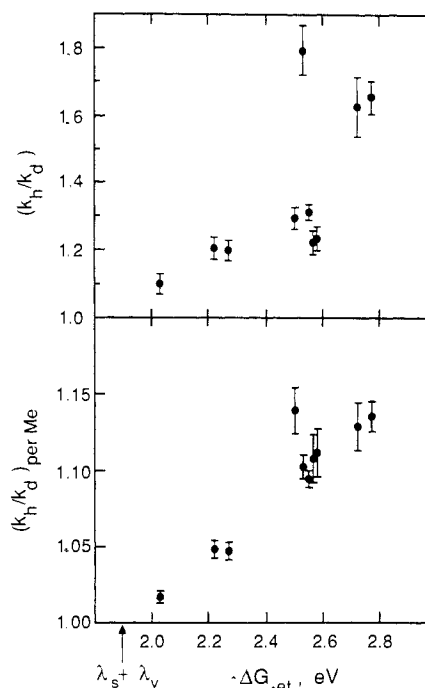
**Table II.** Deuterium Isotope Effect,  $k_h/k_d$ , on the Rates of Return Electron Transfer within Geminate Pairs of TCA Radical Anions and Perdeuteriated or Selectively Deuteriated Alkylbenzene Radical Cations

radical cation	perdeuteriated	methyl deuteriated	ring deuteriated
toluene	1.25 ± 0.04	1.22 ± 0.04	1.00 ± 0.03
<i>p</i> -xylene	1.30 ± 0.03	1.28 ± 0.03	1.01 ± 0.03

on electron-transfer reactions have been reported;<sup>2</sup> however, in several of these cases the origin of the effect is questionable,<sup>3</sup> and no systematic studies for a series of related compounds have been reported yet. Theoretical studies suggest that  $k_h/k_d$  should depend upon the electron-transfer reaction free energy ( $\Delta G_{\text{et}}$ ).<sup>4</sup> Specifically, for pure quantum effects, it is predicted that only normal isotope effects should be observed ( $k_h/k_d > 1$ ), that  $k_h/k_d$  should be approximately unity when the reaction exothermicity is equal to the total reorganization energy (i.e., the sum of the solvent and vibrational reorganization energies,  $\lambda_s + \lambda_v$ ), and that  $k_h/k_d$  should increase as  $\Delta G_{\text{et}}$  increases above  $\lambda_s + \lambda_v$ , i.e., in the Marcus "inverted region".<sup>5</sup> Previous studies, however, have not fully tested these predictions, and, indeed, the inverted region has only recently been observed experimentally.<sup>6</sup> We have reported that return electron transfer within geminate radical ion pairs, eq 1, provides



an excellent example of the inverted region and also that this system is sensitive to small changes in the molecular structure of the ion pairs.<sup>7</sup> We now report the results of the first systematic study of the effect of isotopic substitution on the rates of electron transfer for reactions in the inverted region.



**Figure 1.** Ratios of rate constants for return electron transfer within geminate radical ion pairs of cyanoanthracene radical anions with undeuteriated and perdeuteriated alkyl benzene radical cations in acetonitrile at 25 °C, as a function of the reaction free energy ( $\Delta G_{\text{et}}$ ). In the top half of the figure are plotted the rate ratios ( $k_h/k_d$ ) obtained directly from the experimental data; in the bottom half of the figure the rate ratios are corrected for the number of methyl groups on the benzene donor ( $(k_h/k_d)_{\text{perMe}}$ ).

- (2) (a) Hudis, J.; Dodson, R. W. *J. Am. Chem. Soc.* **1956**, *78*, 911. (b) Zwickel, A. M.; Taube, H. *Discuss. Faraday Soc.* **1960**, *29*, 42. (c) DeChant, J. M.; Hunt, J. B. *J. Am. Chem. Soc.* **1967**, *89*, 5988. (d) Chang, R.; Coombe, R. *J. Phys. Chem.* **1971**, *75*, 447. (e) Kihara, T.; McCray, J. A. *Biochim. Biophys. Acta* **1973**, *292*, 297. (f) Itzkowitz, M. M.; Nordmeyer, F. R. *Inorg. Chem.* **1975**, *14*, 2124. (g) Nakabayashi, S.; Itoh, K.; Fujishima, A.; Honda, K. *J. Phys. Chem.* **1983**, *87*, 5301. (h) Guarr, T.; Buhks, E.; McLendon, G. *J. Am. Chem. Soc.* **1983**, *105*, 3763. (i) Okamura, M. Y.; Feher, G. *Proc. Natl. Acad. Sci. U.S.A.* **1986**, *83*, 8152. (j) Yamataka, H.; Fujimura, N.; Kawafuji, Y.; Hanafusa, T. *J. Am. Chem. Soc.* **1987**, *109*, 4305.
- (3) Guarr, T.; McLendon, G. *Coord. Chem. Rev.* **1985**, *68*, 1.
- (4) (a) Buhks, E.; Bixon, M.; Jortner, J.; Navon, G. *J. Phys. Chem.* **1981**, *85*, 3759. (b) Buhks, E.; Bixon, M.; Jortner, J. *J. Phys. Chem.* **1981**, *85*, 3763.
- (5) (a) Marcus, R. A. *J. Chem. Phys.* **1956**, *24*, 966. (b) Marcus, R. A. *Annu. Rev. Phys. Chem.* **1964**, *15*, 155.
- (6) (a) Miller, J. R.; Beitz, J. V.; Huddleston, R. K. *J. Am. Chem. Soc.* **1984**, *106*, 5057. (b) Closs, G. L.; Calcaterra, L. T.; Green, N. J.; Penfield, K. W.; Miller, J. R. *J. Phys. Chem.* **1986**, *90*, 3673. (c) Wasielewski, M. R.; Niemi, M. P.; Svec, W. A.; Pewitt, E. B. *J. Am. Chem. Soc.* **1985**, *107*, 1080. (d) Irvine, M. P.; Harrison, R. J.; Beddard, G. S.; Leighton, P.; Sanders, J. K. M. *Chem. Phys.* **1986**, *104*, 315.
- (7) (a) Gould, I. R.; Ege, D.; Mattes, S. L.; Farid, S. *J. Am. Chem. Soc.* **1987**, *109*, 3794. (b) Gould, I. R.; Moser, J. E.; Ege, D.; Farid, S. *J. Am. Chem. Soc.* **1988**, *110*, 1991.

Rates of return electron transfer within geminate radical ion pairs of 9,10-dicyanoanthracene (DCA) and 2,6,9,10-tetracyanoanthracene (TCA) radical anions and the radical cations of perdeuteriated methyl-substituted benzene derivatives,  $k_d$ , were determined by using the method previously described.<sup>7</sup> The rates are summarized in Table I together with the corresponding rates for radical ion pairs of the undeuteriated parent donors,  $k_h$ , which were reported previously.<sup>7b</sup> The free energies of the electron-transfer reactions for both sets of ion pairs were calculated by using the relation  $\Delta G_{\text{et}} = E_{\text{red}}(\text{A}) - E_{\text{ox}}(\text{D})$ .<sup>8</sup> For both sets of radical-ion pairs, the rates of the electron-transfer reactions decrease with increasing reaction exothermicity, as expected for reactions in the inverted region.<sup>5,7</sup> In each case, however, the reactions with deuteriated radical cations are slower than the

(8) The oxidation potentials of the deuteriated and undeuteriated donors were assumed to be identical since it has been shown that the effect of deuteriation is to increase the oxidation potentials of substituted benzenes by only ca. 5 mV, which is negligible on the energy scale of Figure 1 (ref 9a).

corresponding reactions of the undeuterated radical cations,  $k_h > k_d$ .

Of particular interest is the effect of selective isotopic substitution. As shown in Table II, for toluene and *p*-xylene, ring deuteration leads to no or insignificant isotope effect, whereas methyl deuteration results in almost the same isotope effect as perdeuteration. These remarkable specific isotope effects are similar to others observed previously in charge-transfer complex absorption spectra<sup>9a</sup> and in the nonradiative decay of exciplexes in the gas phase.<sup>9b-g</sup> The methyl-specific isotope effect is consistent with significant changes in the methyl carbon-hydrogen and ring carbon-methyl carbon bond lengths upon ionization of the substituted benzene.<sup>9</sup> These specific bond length changes are consistent with significant hyperconjugative stabilization of the substituted benzene radical cations by the ring methyl groups.<sup>9a,d-g</sup>

The observed kinetic isotope effect (Table I) seems to depend on the reaction exothermicity and on the number of methyl groups on the benzene ring. Thus, isotope effects per methyl group,  $(k_h/k_d)_{\text{per Me}}$ , are calculated with eq 2 in which  $n$  is the number of methyl groups on the donor.

$$(k_h/k_d)_{\text{per Me}} = (k_h/k_d)^{1/n} \quad (2)$$

In Figure 1 are plotted  $(k_h/k_d)$  and  $(k_h/k_d)_{\text{per Me}}$  as a function of reaction free energy. The plots clearly show that the magnitude of the isotope effect increases with increasing reaction exothermicity ( $\Delta G_{\text{et}}$ ). Previously, we have shown that the maximum rate of return electron transfer for the undeuterated donors, i.e., the rate for which the Franck-Condon factors are maximized and the reaction activation energy is minimized, occurs for a reaction exothermicity of 1.9 eV. According to the figure, at this value of  $\Delta G$ , the  $k_h/k_d$  ratio approaches a value of unity. This observation is in clear agreement with the theoretical predictions of Jortner et al. for isotopic quantum effects.<sup>4</sup> The Franck-Condon factors for the electron-transfer process are reduced as a result of changes in the frequencies of the rearranged vibrational modes. In addition to the frequency changes, the extent of hyperconjugation should decrease with deuteration due to the stronger C-D bond, and thus the internal reorganization could decrease. Thus, the isotope effects observed here could also contain contributions from changes in the internal reorganization energy,  $\lambda_r$ .

Many treatments of electron-transfer reactions assume that the rearranged vibrational modes can be approximated by a single average vibrational frequency, often ca. 1500  $\text{cm}^{-1}$  which is typical of carbon-carbon skeletal stretching modes.<sup>6,7</sup> However, the present deuterium isotope effects suggest that higher frequency modes may have to be taken into account. Indeed, in the radiationless transitions of the triplet states of aromatic hydrocarbons in the gas phase, the role of high-frequency (ca. 3000  $\text{cm}^{-1}$ ) carbon-hydrogen modes is well established, although for these processes, isotope effects are observed upon deuteration of the ring hydrogens.<sup>11</sup> Although the present results do not say anything about lower frequency modes, they suggest that contributions of the high-frequency carbon-hydrogen modes to the single averaged frequency in single mode models should not be underestimated, at least for the reactions of alkyl-substituted aromatic radical cations, in which hyperconjugation can be significant.

**Acknowledgment.** We thank Roger Moody and Bruce Armitage for technical assistance, and Professor W. Saunders, Jr., of the University of Rochester for helpful discussions.

(9) (a) Martens, F. W.; Verhoeven, J. W.; De Boer, T. J. *Tetrahedron Lett.* **1979**, 31, 2919. (b) Dresner, J.; Prochorow, J.; Sobolewski, A. *Chem. Phys. Lett.* **1978**, 54, 292. (c) Prorochow, J.; Deperasinska, I.; Sobolewski, A. *J. Lumin.* **1979**, 18/19, 105. (d) Lim, B. T.; Okajima, S.; Chandra, A. K.; Lim, E. C. *J. Chem. Phys.* **1982**, 77, 3902. (e) Okajima, S.; Lim, E. C. *J. Phys. Chem.* **1982**, 86, 4120. (f) Lim, B. T.; Okajima, S.; Chandra, A. K.; Lim, E. C. *Chem. Phys. Lett.* **1981**, 79, 22. (g) Okajima, S.; Lim, B. T.; Lim, E. C. *J. Chem. Phys.* **1980**, 73, 3512.

(10) Howell, J. O.; Gonclaves, J. M.; Amatore, C.; Klasinc, L.; Wightman, R. M.; Kochi, J. K. *J. Am. Chem. Soc.* **1984**, 106, 3968.

(11) Henry, B. R.; Siebrand, W. In *Organic Molecular Photophysics*; Birks, J. B., Ed.; Wiley: New York, 1973; p 153.

## Hydrogen-Deuterium Exchange of Diborane in Superacid Solution through Diboranonium ( $\text{B}_2\text{H}_7^+$ ) and Diboranium ( $\text{B}_2\text{H}_5^+$ ) Ions<sup>1a,b</sup>

George A. Olah,\* Robert Aniszfeld, G. K. Surya Prakash, and Robert E. Williams

Donald P. and Katherine B. Loker Hydrocarbon Research  
Institute and Department of Chemistry  
University of Southern California  
Los Angeles, California 90089-1661

Koop Lammertsma\* and Osman F. Güner

Department of Chemistry, University of Alabama at  
Birmingham, Birmingham, Alabama 35294

Received August 3, 1988

The gaseous positive ion chemistry of diborane **1** was studied by mass spectrometry, including ICR studies.<sup>2</sup> Aside from the preparation of simple carborane cations,<sup>3,4</sup> the behavior of diborane **1** in superacidic media has not been previously explored, although the interaction of  $\text{B}_2\text{H}_6$  with  $\text{HF}(\text{DF})$  was the subject of theoretical<sup>5</sup> and spectroscopic studies.<sup>6</sup> We report herein the slow proton/deuterium exchange of  $\text{B}_2\text{H}_6$ , **1**, in the superacidic  $\text{FSO}_3\text{D}\cdot\text{SbF}_5$  (deuterio Magic acid)/ $\text{SO}_2\text{ClF}$  medium at low temperatures involving the corresponding isotopomeric diboranonium ions (protonated diborane)  $\text{B}_2\text{H}_7^+$  ions. The structure of the  $\text{B}_2\text{H}_7^+$  ion has also been probed by ab initio theoretical calculations.

When triply distilled diborane, ( $\text{B}_2\text{H}_6$ ) **1**,<sup>7</sup> was mixed with 1:1  $\text{FSO}_3\text{D}\cdot\text{SbF}_5$  (deuterio Magic acid)/ $\text{SO}_2\text{ClF}$  at  $-78^\circ\text{C}$ , most of the diborane dissolved with no detectable gas evolution, and a colorless solution was obtained. An immediate  $^{11}\text{B}$  and  $^2\text{H}$  NMR<sup>8</sup> analysis did not reveal any initial proton-deuterium exchange. After 24 h, however, at  $-78^\circ\text{C}$ , such analysis showed proton-deuterium exchange. Direct NMR study of the superacidic solution of diborane did not reveal the presence of any observable cation and was indicative only of a complex mixture of exchanged boranes. After warming to room temperature analysis of the products also showed the formation of some  $\text{BF}_3$  and  $\text{H}_2$  as well as  $\text{SO}_2$  and  $\text{SbF}_5$ . By using standard vacuum line techniques, a portion of diborane was removed and condensed onto frozen THF. Upon warming, the thawed THF solution was subjected to  $^2\text{H}$  NMR spectroscopic analysis. The proton decoupled  $^2\text{H}$  NMR showed a peak at 2.5 ppm indicating proton-deuterium exchange in  $\text{B}_2\text{H}_6$ . The peak at 2.5 ppm is identical with that of  $\text{THF}\cdot\text{BD}_3$  obtained by reacting  $\text{B}_2\text{D}_6$  with THF. Partially exchanged diboranes ( $\text{B}_2\text{H}_5\text{D}$  to  $\text{B}_2\text{HD}_2$ ) which form  $\text{THF}\cdot\text{BD}_2\text{H}$  and  $\text{THF}\cdot\text{BDH}_2$  adducts also show similar  $^2\text{H}$  NMR spectra. In a further experiment a gas-phase sample was also subjected to FT-infrared analysis.<sup>9</sup> The spectrum obtained is complex as would be expected from a  $\text{B}_2\text{H}_6$ ,  $\text{B}_2\text{H}_5\text{D}$ , etc. mixture wherein the deuterium is at

(1) (a) Onium Ions. 37. At the the University of Southern California. For Part 36, see: Olah, G. A.; Prakash, G. K. S.; Marcelli, M.; Lammertsma, K. *J. Phys. Chem.* **1988**, 92, 878. (b) Dedicated to Professor Heinz Nöth on occasion of his 60th birthday.

(2) Dunbar, R. C. *J. Am. Chem. Soc.* **1968**, 90, 5676.

(3) Olah, G. A.; Prakash, G. K. S.; Williams, R. E.; Field, L.; Wade, K. *Hypercarbon Chemistry*; Wiley Interscience: New York, NY, 1987.

(4) Williams, R. E.; Prakash, G. K. S.; Field, L. D.; Olah, G. A. *Advances in Boron and the Boranes*; Liebman, J. F., Greenberg, A., Williams, R. E., Eds.; VCH Publishers, Inc.: New York, 1988, p 191.

(5) Rowlands, T. W.; Somasundram, K. *Chem. Phys. Lett.* **1987**, 135, 549.

(6) Gutowsky, H. S.; Emilsson, T.; Keen, J. D.; Klots, T. D.; Chang, C. *J. Chem. Phys.* **1986**, 85, 683.

(7) Diborane was prepared from the reaction of sodium borohydride (or deuteride) and sulfuric acid (or deuteriosulfuric acid) by Weiss and using the procedure described by Shapiro (Weiss, H. G.; Shapiro, I. *J. Am. Chem. Soc.* **1959**, 81, 6167).

(8) The NMR spectra was recorded on a Varian Associates VXR 200 MHz NMR spectrometer equipped with variable temperature broad band probe.

(9) The infrared spectra was recorded on a Perkin-Elmer 1500 FT-IR instrument. The gas cell used was 10 cm long.